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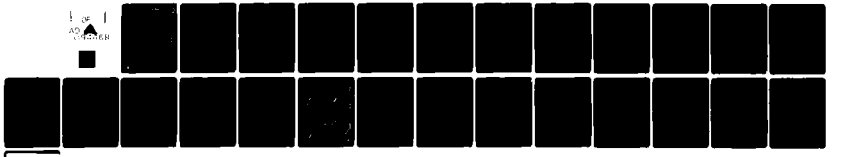

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A Novel Device for the Accurate Dispensing of Small Volumes of Liquid Samples.

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Washington, D.C.

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droplet generation
microsampling
sample dispenser

A sample dispenser with electronic control of delivered volume has been designed and evaluated. With the new device, liquid samples are dispensed in the form of uniform droplets less than 4 nL in volume; total volumes as small as 40 nL can be delivered with 1.5% precision. Important features of the microdroplet formation process have been studied and the effect of sample solution concentration and viscosity have been examined. The new dispenser is expected to find application in several areas, including electrothermal atomization atomic absorption spectrometry, automated titrimetry, and high-precision, low-volume solution sampling.

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TECHNICAL REPORT NO. 32

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by

J. G. Shabushnig and G. M. Hieftje

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ANALYTICA CHIMICA ACTA

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SUMMARY

A sample dispenser with electronic control of delivered volume has been designed and evaluated. With the new device, liquid samples are dispensed in the form of uniform droplets less than 4 nL in volume; total volumes as small as 40 nL can be delivered with 1.5% precision. Important features of the microdroplet formation process have been studied and the effect of sample solution concentration and viscosity have been examined. The new dispenser is expected to find application in several areas, including electrothermal atomization atomic absorption spectrometry, automated titrimetry, and high-precision, low-volume solution sampling.

INTRODUCTION

Many analytical techniques require the accurate and precise application or delivery of small volumes of liquid samples. In order to meet these needs, various syringe-based dispensers have been designed [1-3]. However, these devices are generally limited to delivering volumes of 1 µL or larger and are not amenable to rapid, electronic control of the volume dispensed. They often suffer also from irreproducible transfer of the sample to a surface, such as that of an electrothermal atomizer [4].

Tiny samples in the form of microdroplets, typically 50-100 µm in diameter, were used by several researchers in the study of atomization processes in chemical flames [5-7], and as a means of sample introduction

for quantitative analysis [8]. Microdroplets have also been employed for titrant delivery in micro-titrations [9,10].

The use of a microdroplet generator for sample delivery is attractive primarily because of the wide range of volumes which can be accurately dispensed and the ease with which this volume can be controlled by varying the number of droplets generated. Unfortunately, most devices used to generate microdroplets are not convenient to use and require substantial bulk volumes from which the droplets are extracted. Such devices form droplets by forcing the desired solution through a vibrating capillary or orifice and sonically decomposing the resulting jet into a stream of droplets. This method requires relatively large amounts of sample solution, is prone to failure from capillary clogging, and expells microdroplets with considerable velocity, making them hard to control and encouraging droplet splashing or shattering.

In order to overcome these difficulties, we have designed a new kind of droplet-generator-based sample dispenser after the method described by Abbott and Cannon [11]. This system, shown in operation in Fig. 1, generates microdroplets by rapidly withdrawing a glass stylus from an aliquot of sample solution contained in a suitable reservoir. As the stylus withdraws, it pulls with it a filament of solution from the reservoir. Upon further withdrawal of the stylus, the filament detaches itself first from the stylus, and then from the bulk of solution remaining in the reservoir. This filament then collapses upon itself, forming a microdroplet which falls freely from the apparatus. The microdroplets fall in a reproducible trajectory and are easily collected on a surface or in a container.

In this paper, the utility of this device for sample dispensing and application is evaluated. It is demonstrated that sample volumes as small as 40 nL can be reliably dispensed, and sample delivery rates can range from the application of a single 40 nL volume in 0.7 sec to sample flows of 36 µL/min. At present, sample delivery precision is known to be at least as good as 1.5% relative standard deviation for volumes greater than 40 nL. Unfortunately, measurement uncertainty currently precludes a better estimate of precision. Potential areas of application of the new apparatus are considered and its limitations discussed; the system is expected to be especially useful where small total volumes of sample material are available and where sample delivery precision is critical.

EXPERIMENTAL

Instrument description

A schematic diagram of the new sample dispenser is shown in Fig. 2, with the specific components listed in Table 1. The stylus is solid, drawn borosilicate glass with a main shaft 0.5 mm in diameter x 30 mm long and a tip 120 µm in diameter x 10 mm long. These specific dimensions are not critical, but have proven convenient in routine use. The stylus is driven by a ceramic piezoelectric bimorph mounted in a cantilever configuration. The stylus is affixed to the bimorph with epoxy cement and can be accurately positioned with respect to the reservoir by means of a vertical screw translator.

The bimorph itself is driven by an amplifier supplying a 100 V peak-to-peak sine wave at 157 Hz, the resonant frequency of the bimorph–stylus com-

bination. It is necessary to operate this system at resonance in order to produce sufficient deflection of the stylus for microdroplet formation. The influence of operating frequency on stylus deflection is clearly shown in Fig. 3.

The reservoir tube used in the present study is a 4-cm long section of 2-mm i.d. glass tubing which holds the sample solution by capillary action. If a large sample volume is to be employed or many repetitive volumes of the same solution are to be dispensed, the reservoir tube can be coupled to a larger vessel through a siphon.

The baffle is a 25-mm section of 6-mm i.d. glass tubing placed through the center of a 40-mm diameter aluminum disk. This combination serves to shield the falling microdroplets from air currents about the apparatus, making their trajectory and therefore the location of sample deposition more reproducible.

An electronic gate allows the operator to select the exact number of microdroplets which are dispensed. Each cycle of the bimorph driving wave produces a single microdroplet. In turn, the number of driving wave cycles is controlled by a preset value in the gate controller, which opens the gate between the wave form generator and amplifier for the requisite number of cycles. In routine use, the volume which is dispensed is related to the number of bimorph driving cycles through a calibration curve or measured droplet volume. This hardware scheme could easily be duplicated under software control with a small laboratory computer or microprocessor.

The ceramic bimorph exhibits a significant level of hysteresis upon start up, causing the initial 100 droplets (200-400 nL total volume) to be

formed with [illegible] reproducibility. Fortunately, acceptable precision ([illegible]) can be restored by discarding the microdroplets for [illegible] the first 100 cycles. The microdroplets are discarded by a jet of air which blows them into a trap. After the initial 100 cycles the [illegible] is terminated, allowing the remainder of the microdroplets to be [illegible] The air jet is synchronized with the gate controller and [illegible] p.s.i.g. of air pressure to operate reliably.

Assessment of [illegible] accuracy

Several [illegible] were employed to determine the volume of a single microdroplet [illegible] the reproducibility of droplet volume, and to examine the effect of experimental variables on droplet size.

Droplet volume and its reproducibility were initially measured indirectly from the diameter of the impression formed by a falling microdroplet in a bed of fine grain magnesium oxide [12]. Such a bed is easily prepared by burning a strip of magnesium ribbon in air and collecting the resulting oxide smoke on a microscope slide. The slide thus prepared was passed through the stream of falling microdroplets, with the resulting impressions viewed under a microscope. The diameters of these impressions were then quantified [illegible] with a standard stage micrometer. To obtain the true droplet diameter, the values so obtained were multiplied by an empirically determined factor of 0.85 [13], to correct for distortion of the microdroplet on impact. This method allows droplet diameters to be determined with an accuracy of ± 0.5 μm and a precision of 1.9% RSD.

A second method was employed to evaluate the accuracy and precision with which aggregates of microdroplets could be dispensed. For these measurements, the reservoir of the microdroplet generator was filled with a solution containing 10 mg Mg mL^{-1}. The dispenser was then used to deliver selected amounts of this "sample" into vials containing 3 mL of deionized water. The concentration of the resulting magnesium solution was determined by atomic absorption spectrometry.

With this latter technique, accuracy of sample dispensing was evaluated by comparing measured magnesium concentrations with those calculated from the known microdroplet size, number of microdroplets dispensed, concentration of original Mg solution, and the volume into which the sample was delivered.

The major uncertainty in this latter method is in the microdroplet volume measured from magnesium oxide impressions. A ± 0.5 μm uncertainty in diameter generates an approximately 2% uncertainty in volume for the range of microdroplet diameters examined. Other sources of error, propogated through the measurement procedure, raise the overall uncertainty to 3%.

Precision of sample delivery was determined by dispensing 5 replicate samples into measured volumes of water and comparing the resulting Mg concentrations. Measurement of 5 aliquots of the same sample produced 1.0 - 1.5% r.s.d., indicating the limit of this method. Of course these precision values are actually a result of errors in both the dispensing and measurement procedures. The precision of sample delivery might actually be better than the values reported.

RESULTS AND DISCUSSION

Single droplet ejection

The size of ejected picoliter microdroplets is governed by both the stylus diameter and the depth to which it penetrates the bulk liquid in the sample reservoir. Penetration depth is conveniently measured under stroboscopic illumination with a microscope containing a calibrated reticle. The range over which microdroplets can be tuned with a 120-μm diameter stylus is indicated in Fig. 3. As shown, increasing penetration depth results in the production of microdroplets of a larger diameter. Increasing or decreasing the stylus diameter shifts this entire range up or down.

In the present work, microdroplets between 175 - 200 μm are preferred; they are large enough to travel along a reproducible trajectory but still possess a small individual volume for fine resolution in total sample volumes.

Solution viscosity and surface tension strongly affect the size of generated microdroplets. Although no exact relationship between these parameters has yet been developed, Fig. 5 clearly shows an increase in microdroplet diameter with increasing solution viscosity. This behavior arises, presumably, from the formation of a longer, more stable filament from the higher viscosity solution (cf. Fig. 1, frame 4). This longer filament produces a larger microdroplet upon collapse. Also, surface tension influences microdroplet size by altering the "grip" the stylus has on the solution filament. This "grip" affects when detachment of the filament occurs, and therefore influences the size of the resulting microdroplet. Importantly, although these factors affect the size of microdroplets dispensed, and therefore necessitate calibration, a wide range of solution viscosities as well as organic solvents can be conveniently dispensed.

From MgO impression measurements, single microdroplets can be produced with a precision in diameter of 3.3% r.s.d. However, this error propogates to a relative standard deviation of 10% in terms of volume.

Aggregate sample studies

Calibration curves for the sample dispenser operating over two widely different volume ranges are shown in Figs. 6-7. Comparison with calculated values indicates an accuracy of approximately ± 1.5% over both ranges. Typical values for precision, indicated in Tables 2-3, suggest a usable lower limit for volumes dispensed of about 40 nL (with use of air jet).

Figure 6 indicates the importance of using the air-jet droplet deflection system to improve accuracy and precision for sample volumes below 200 nL. The use of the air-jet eliminates roll-off in the calibration curve, restoring an intercept at the origin. The improvement in precision is indicated by Tables 2 and 3. At sample volumes greater than 200 nL the air jet system is not required, as indicated by the convergence of the two portions of Fig. 6.

Although Fig. 7 extends only to 25 µL, larger volumes can be conveniently dispensed. The only limit to larger volumes are reservoir capacity and the maximum count compatible with the gate controller. In the present instrument, both factors can be easily modified to accommodate a larger range of sample volumes if desired.

Droplet charge

In the course of this study on microdroplet formation it was noticed that the microdroplets possess a small inherent charge. The charge was

determined by [illegible] droplet stream between a set of planar copper electrodes [illegible] measuring the resulting deflection. This method yields [illegible] current charge on each microdroplet of 10^{-13} coulombs [illegible] 10^6 electrons.

CONCLUSIONS

A sample [illegible] droplet generator can provide a wide range of [illegible] liter to microliter, under convenient electronic control [illegible] reliable, inexpensive to build, and simple to operate.

This device [illegible] employed to improve precision in sample application to [illegible] atomizer, but should also be useful in microtitration [illegible] where small, reproducible sample aliquots are [illegible]

ACKNOWLEDGEMENT

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Table 1

Instrumental [illegible]

Bimorph:	[illegible] x 0.5" x 0.021" manufactured by [illegible] Piezoelectric Division, Bedford, OH
Waveform generator:	[illegible], based on an EXAR XR-2206 CP [illegible]
Gate:	[illegible] used in conjunction with a 741 operational amplifier
Gate controller:	[illegible], based on 7490 decade counters and [illegible] bit comparators.
Amplifier:	[illegible], 2-stage push-pull amplifier capable [illegible] 300 Vp-p, approximate gain of 75.
Solenoid valve:	[illegible] 12-V solenoid valve manufactured by [illegible] Scientific, East Hanover, NJ.

Table 2

Precision as a function of volume dispensed (no air jet deflection employed)

Volume dispensed(nL)	RSD(%)
7.8	32.5
65	6.0
204	3.4
431	0.6
830	0.4
2,600	1.06
3,900	0.4
7,300	1.5
10,100	1.1
24,600	1.2

Table 3

Precision as a function of volume dispensed with air jet used to deflect initial 100 microdroplets

Volume (nanoliters)	RSD(%)
[illegible]	35.7
19.5	17.3
39.0	6.3
78.0	1.6
234	0.3

FIGURE LEGENDS

Figure 1. Microdroplet formation sequence
(1-3) filament formation
(4) filament detaches from stylus
(5) filament collapse
(6) microdroplet

Figure 2. Schematic diagram of sample dispenser based on a microdroplet generator.

Figure 3. Stylus deflection as a function of bimorph driving frequency (100 V peak-to-peak voltage applied to bimorph).

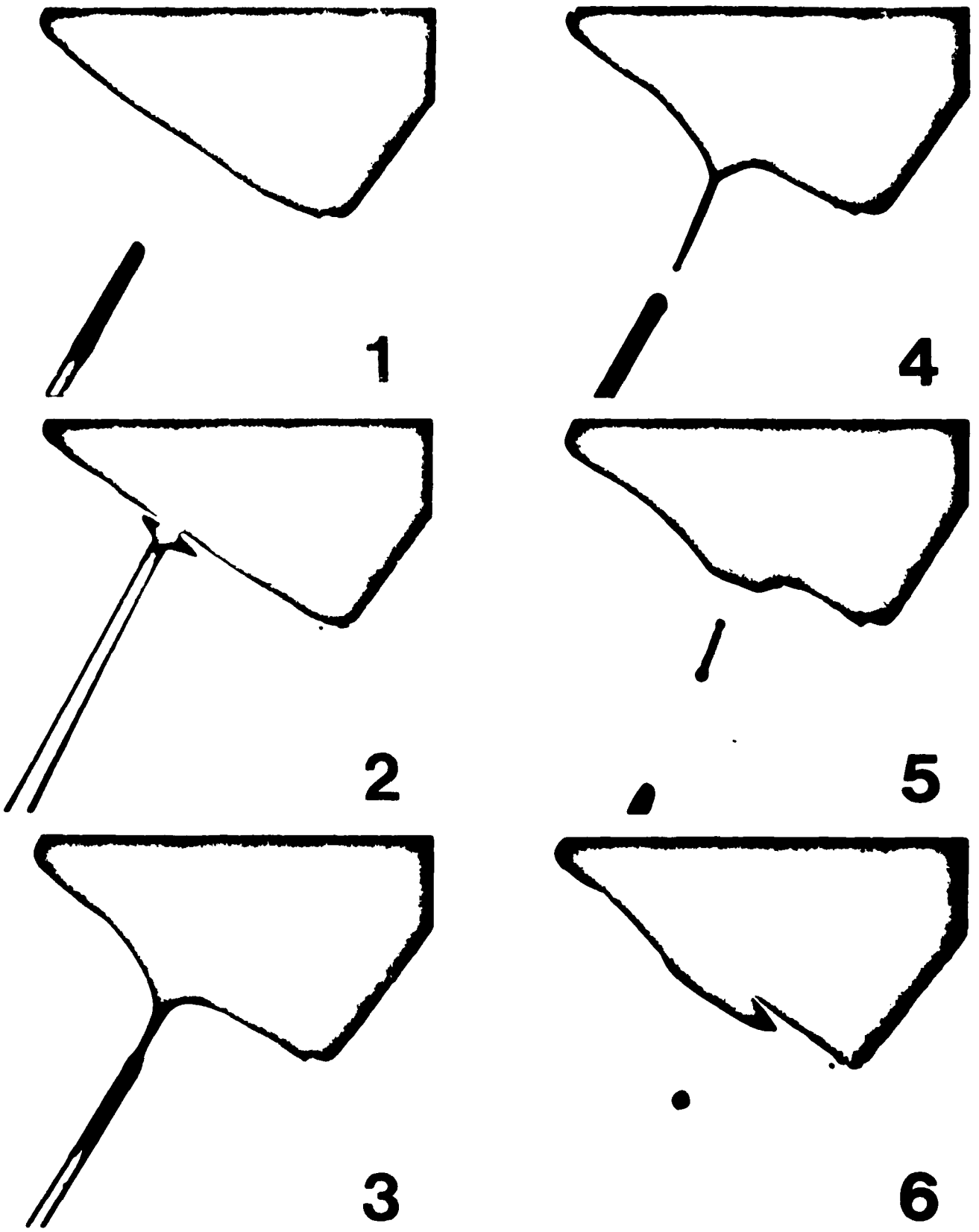
Figure 4. Droplet diameter as a function of depth to which stylus penetrates bulk solution.

Figure 5. Droplet diameter as a function of glycerol concentration in aqueous solution. Range of viscosities across curve is from 1 to 1000 cP (approximately).

Figure 6. Calibration curve for sample dispenser showing effect of the air jet on small volume samples.
(Circles - experimental values with air jet,
triangles - experimental values without air jet).

Figure 7. [illegible] for sample dispenser, 1-25 µL range.

Fig 1



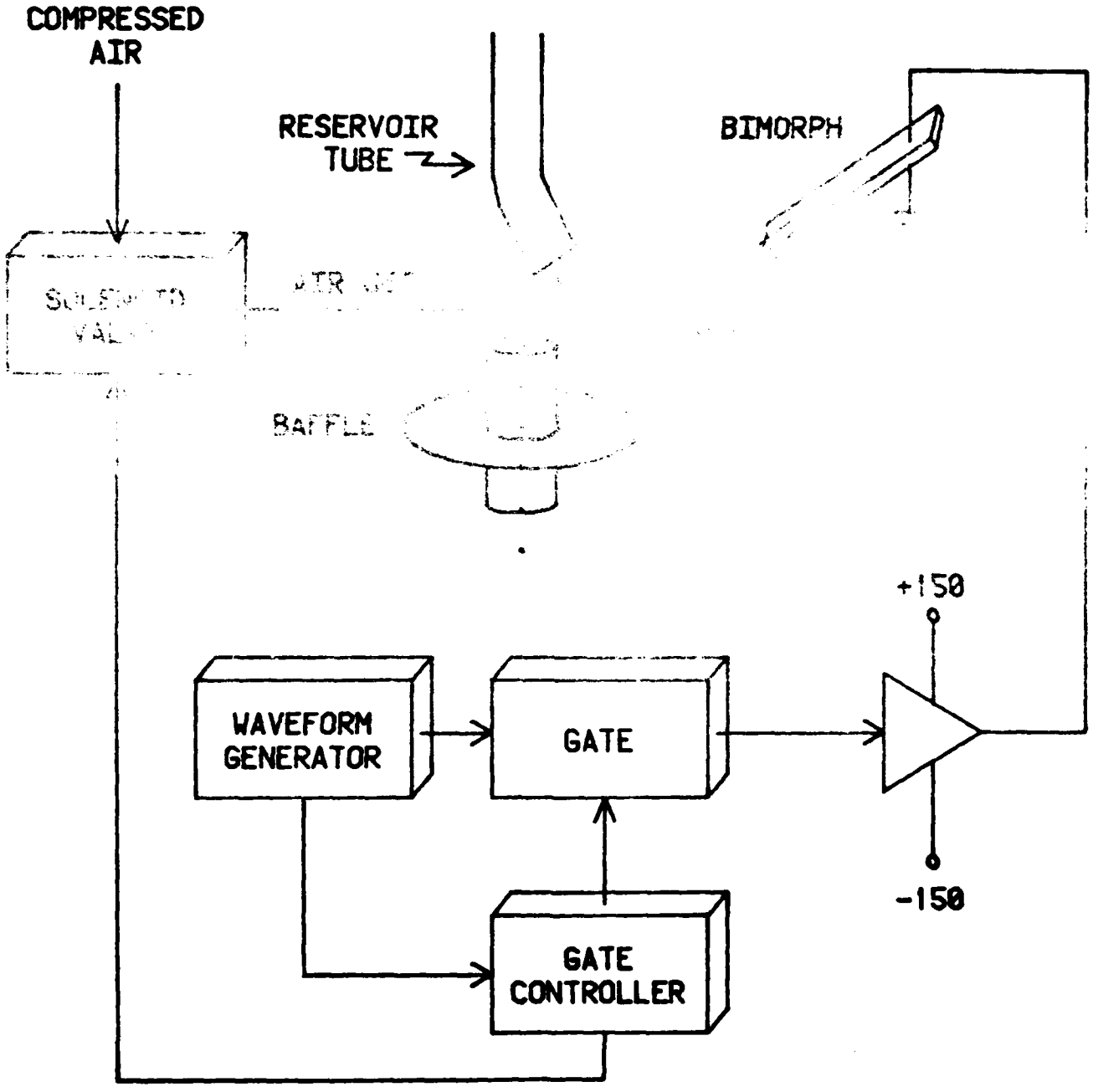
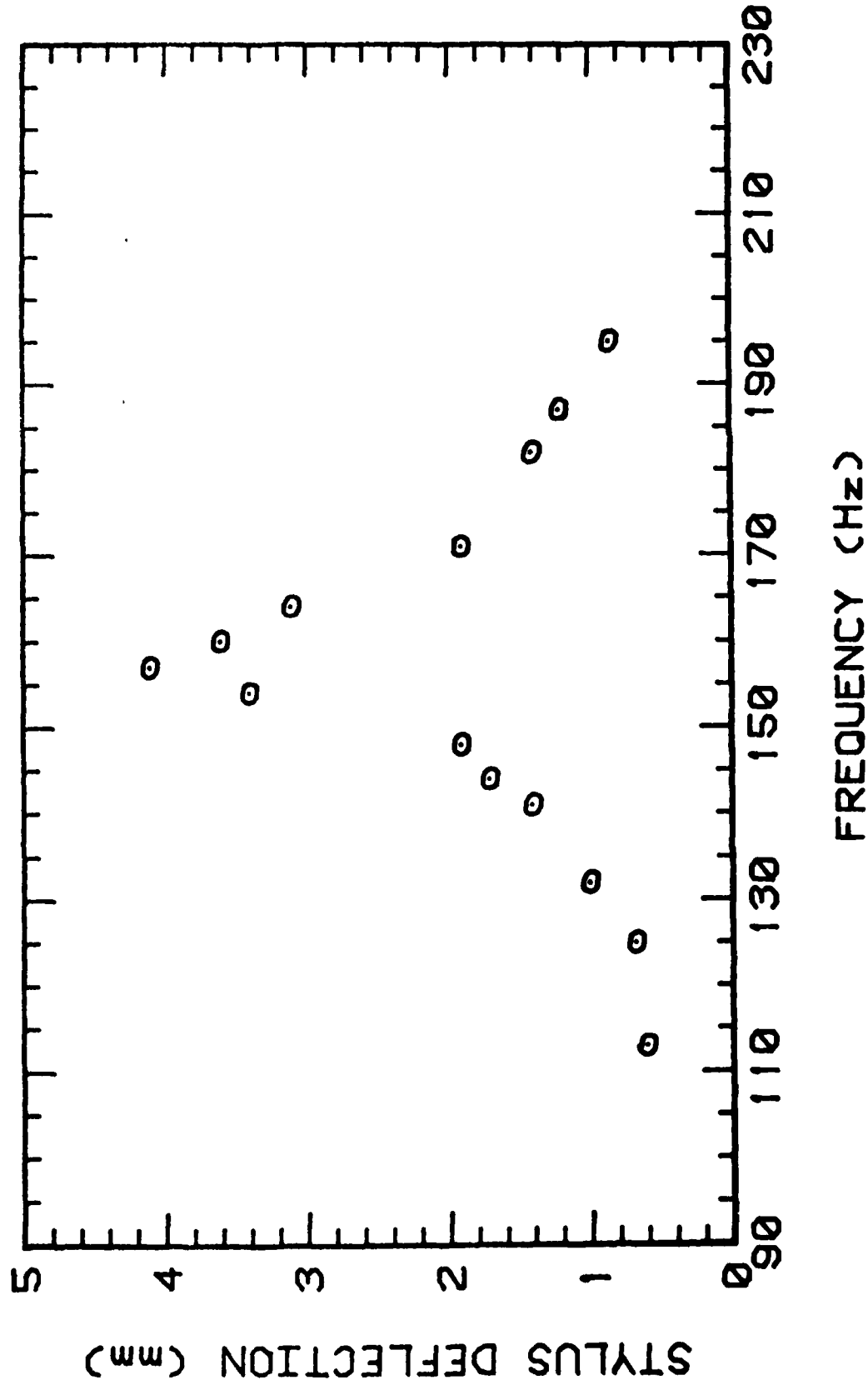

COMPRESSED AIR
RESERVOIR TUBE
BIMORPH
BAFFLE
+150
WAVEFORM GENERATOR
GATE
-150
GATE CONTROLLER

Fig. 3


STYLUS DEFLECTION (mm)
5
4
3
2
1
0
FREQUENCY (Hz)
90
110
130
150
170
190
210
230

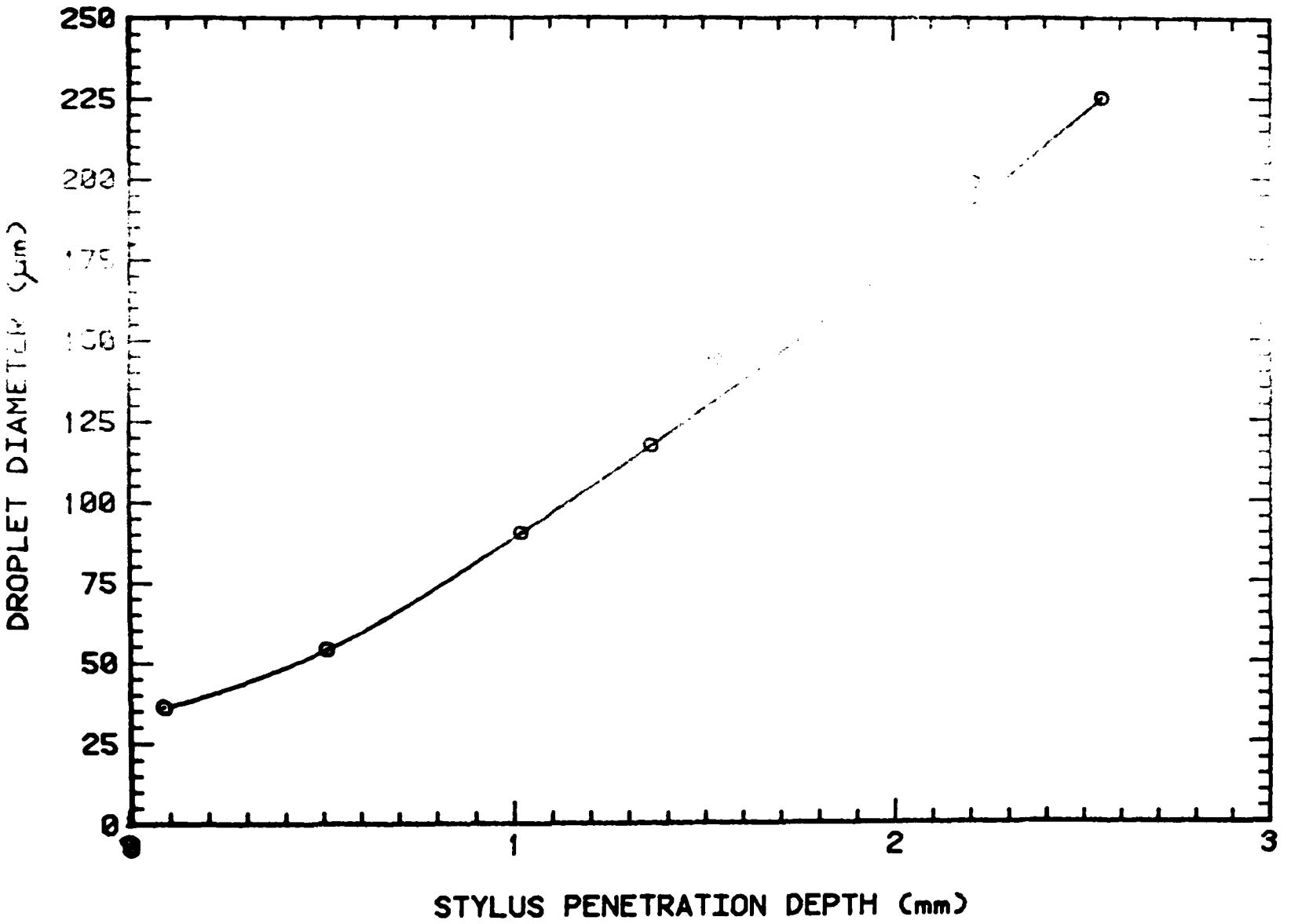

250
225
200
175
150
125
100
75
50
25
0
DROPLET DIAMETER (μm)
1
2
3
STYLUS PENETRATION DEPTH (mm)

Fig. 4

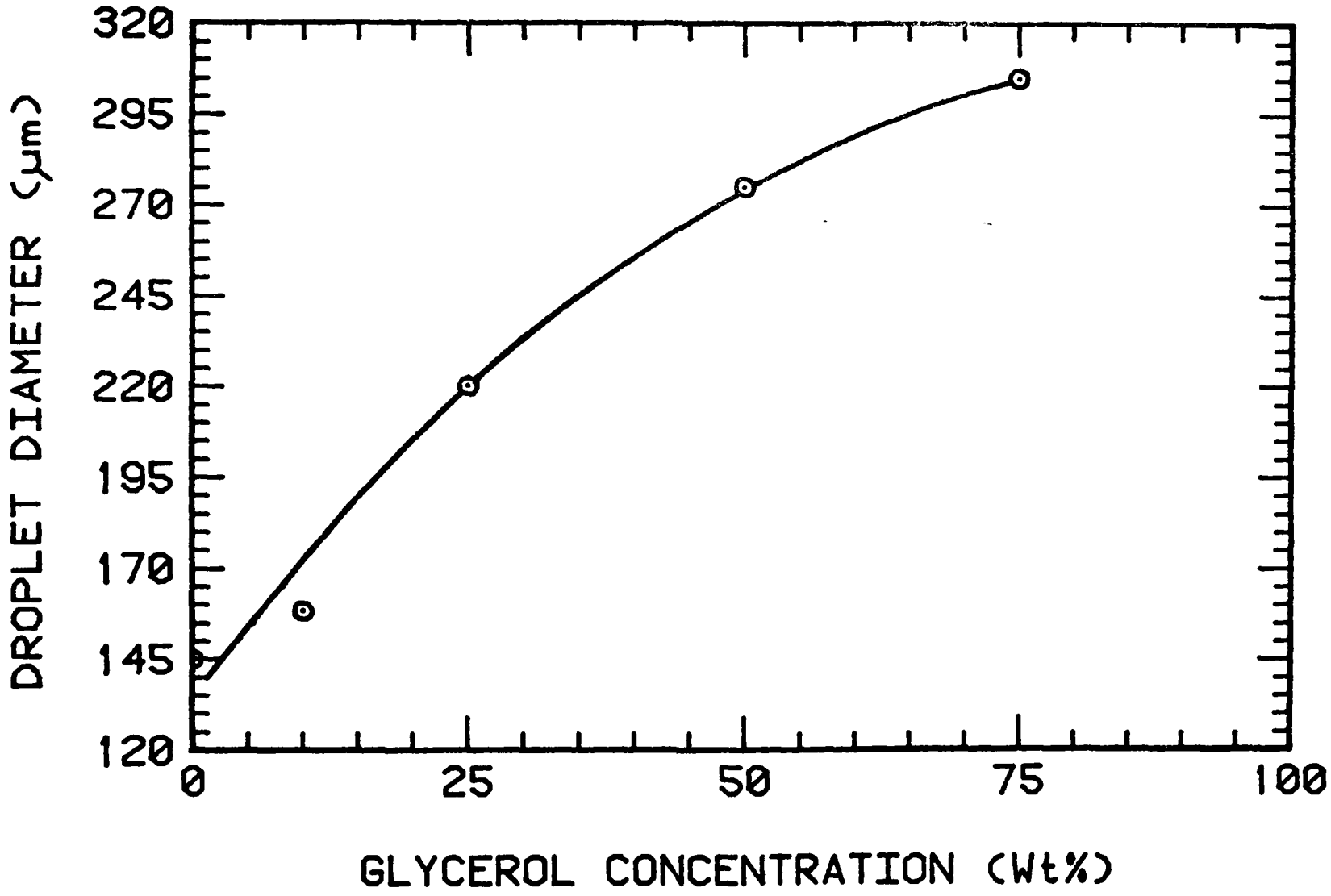
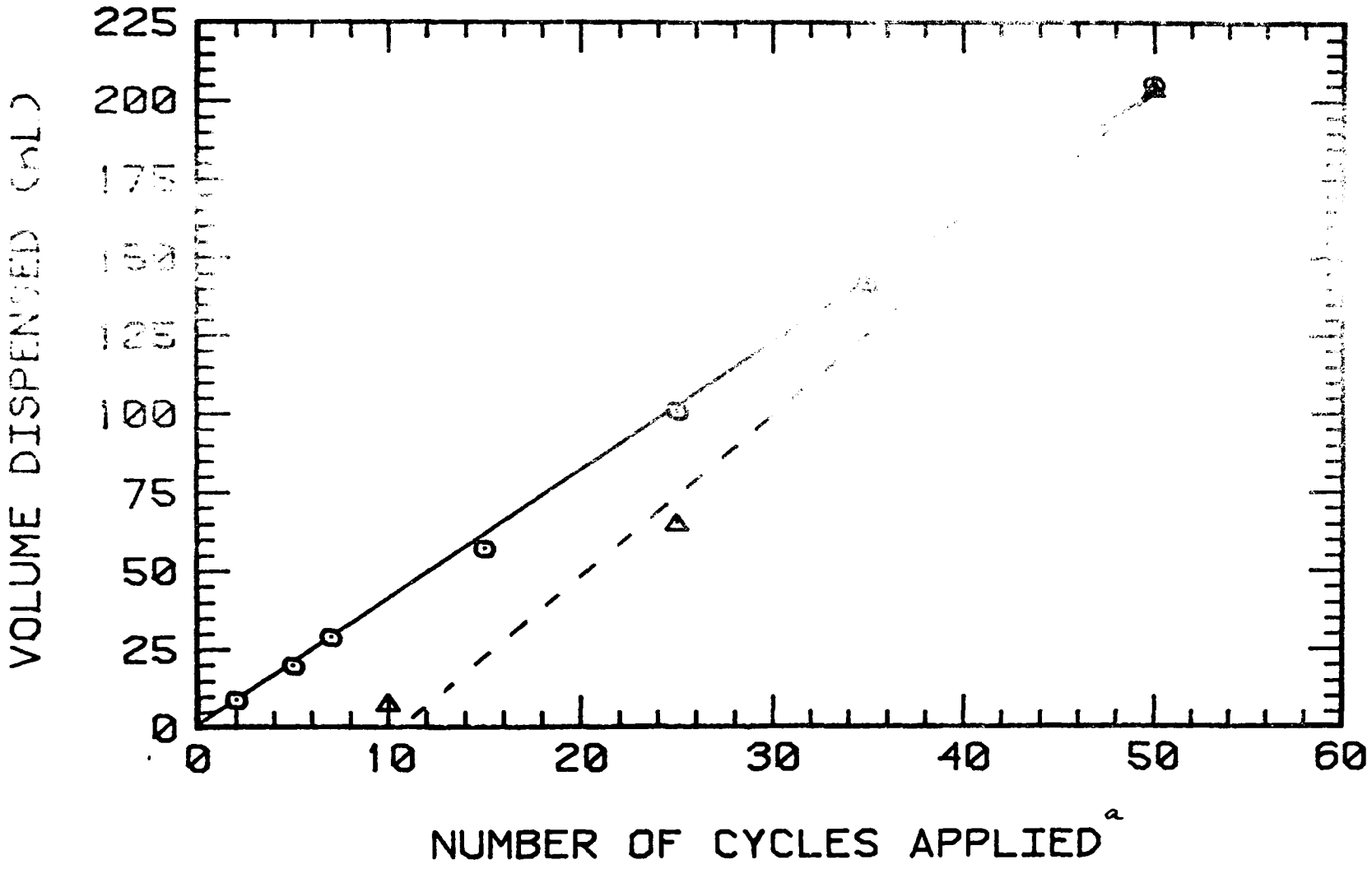

320
295
270
245
220
195
170
145
120
DROPLET DIAMETER (μm)
0
25
50
75
100
GLYCEROL CONCENTRATION (Wt%)

Fig. 5



a. Number of cycles after

Fig 6

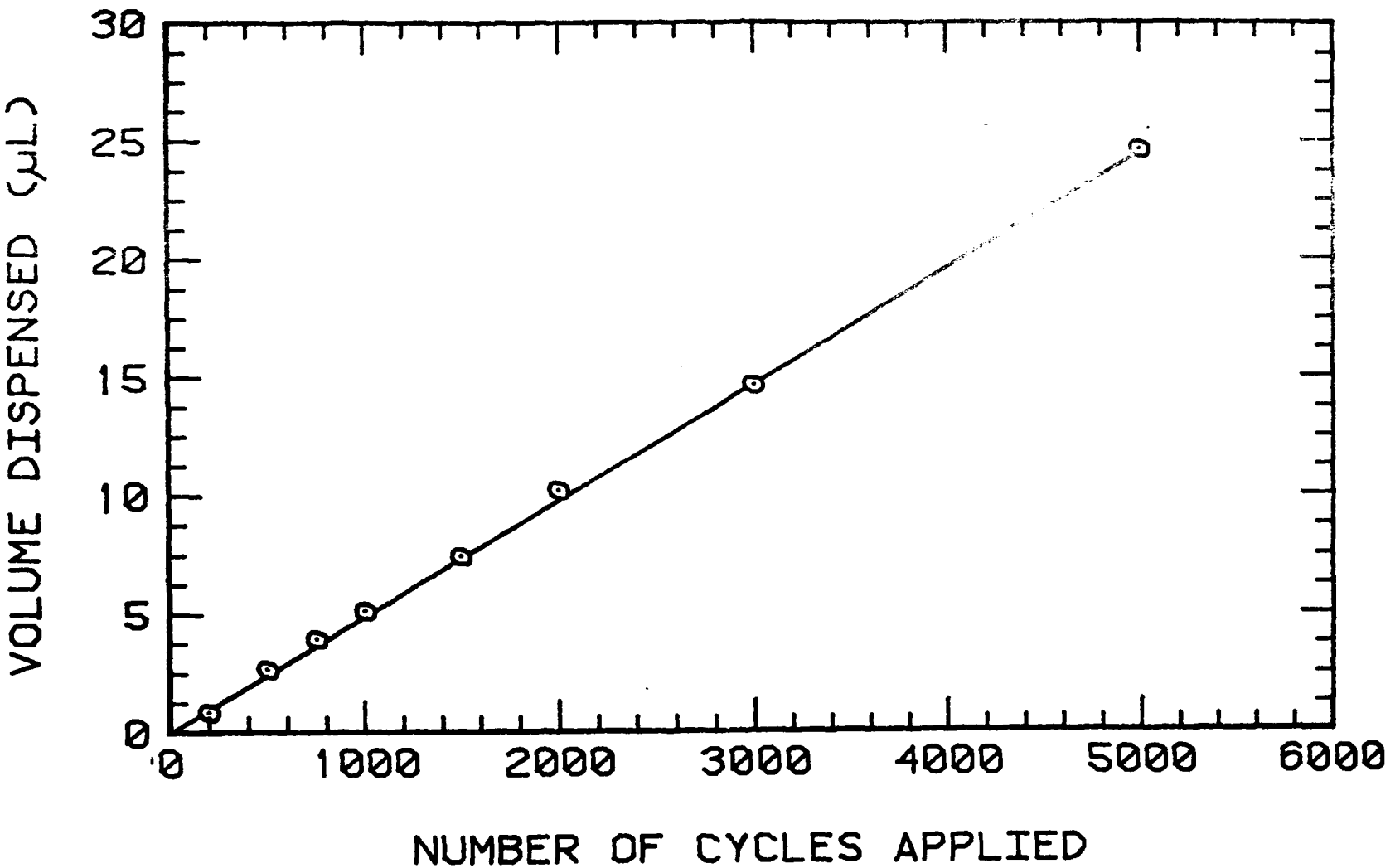

VOLUME DISPENSED (µL)
30
25
20
15
10
5
0
0
1000
2000
3000
4000
5000
6000
NUMBER OF CYCLES APPLIED

Fig. 7

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